# Photoluminescent properties of lead zirconate powders obtained by the polymeric precursor method

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## Abstract

Lead zirconate powders, obtained by the polymeric precursor method, were annealed for 2 h at temperatures from 300 to 800 °C. The effect of heat treatment on structural defects and photoluminescent behavior was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Fourier transform Raman spectroscopy (FT-Raman), scanning electron microscopy (SEM), and photoluminescence spectroscopy (PL). XRD patterns and FT Raman spectra showed that the structure of the $PbZrO_3$ powders was orthorhombic. FT-IR spectra exhibited absorption bands at 450 and 860 cm$^{-1}$. These were ascribed to Zr–O bands and indicate the $ZrO_6$ octahedral group. SEM micrographs suggested that the annealing temperature allowed structural morphology changes in the samples. $PbZrO_3$ powders emitted green photoluminescence at room temperature and at lower annealing temperatures but no photoluminescence was observed from the ordered structure. This optical behavior was attributed to structural evolution from disordered to ordered as a function of $PbZrO_3$ powder annealing. The intensity of the green PL component increased after annealing at 300 °C.
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## 1. Introduction

Perovskite-type compounds belong to a class of materials that have been investigated extensively since the 1940s due to their significance in fundamental research and high potential for technological applications [1]. The general formula of a perovskite compound is $ABO_3$ (where A = Ca, Sr, Pb or Ba and B = Ti or Zr). These are among the most important materials due to their electronic, ferroelectric and optical properties. Furthermore, they are some of the most versatile for chemical tuning of composition and structure. These materials display a plethora of physical and chemical properties of technological interest that depend on processing conditions, oxygen content, and order [1–6].

Interest in this kind of material is great because disordered semiconductors can replace single crystal semiconductors in many optoelectronic devices, especially regarding photoluminescent properties [7–11]. Our group has investigated a number of diverse structurally disordered materials, including the properties of perovskite-type compounds, such as $BaTiO_3$ [12], $CaTiO_3$ [13–15], $PbTiO_3$ [16,17], $BaZrO_3$ [18,19], $SrZrO_3$ [20] and $BaSrTiO_3$ [21].

Diverse theories in the literature indicate that the visible wide-band emissions observed in titanates belong to a universal green luminescence which is a characteristic property of practically all self-activated $ABO_3$ perovskite titanates [22]. Its origin has been explained and discussed in many papers. The mechanisms suggested in the literature include self-trapped excitons [23], recombination of electron and hole polarons and a charge transfer vibronic exciton [24], donor–acceptor recombination [25] and transitions in $MeO_6$ complexes [26].

The photoluminescent (PL) emission band of $ABO_3$ perovskites prepared by the polymeric precursor method is

directly linked to the degree of structural order–disorder in the lattice, as well as to preparation method and thermal treatment conditions [27,28]. The optical properties of the amorphous semiconductors are dominated by the presence of an optical absorption tail that falls exponentially in the region and is usually transparent in crystalline solids. This is referred to as the absorption edge and is attributed to the presence of localized states in the typical band gap of amorphous semiconductors [29,30].

New studies describe the preparation and analysis of $Ba(Zr_xTi_{1-x})O_3$ (BZT) ceramic or thin films as a replacement for $BaTiO_3$. This is desirable since the $Zr^{4+}$ ion is chemically more stable than the $Ti^{4+}$ ion [31,32]. Recently, doped $PbZrO_3$ (PZT) has been chosen as an alternative material for the fabrication of ceramics and thin films by conventional solid state reaction and sol gel methods in order to analyze the antiferroeletric properties of this material [33,34].

In this study, $PbZrO_3$ (PZ) powders were synthesized by the polymeric precursor method (PPM), annealed at different temperatures (300–800 °C for 2 h) and analyzed to determine visible photoluminescence of amorphous and crystalline PZ powders at room temperature. The PZ powders were synthesized by soft chemical processing and analyzed by SEM, XRD, FT-IR, FT-Raman, PL spectra and PL curve decomposition into Gaussian peaks. The crystalline and disordered structures of the samples were confirmed by the previously mentioned techniques and corresponding photo-luminescence properties were measured. Only the structurally disordered samples displayed visible PL at room temperature.

## 2. Experimental

PZ powders were prepared by the soft chemical polymeric precursor method (PPM) [35], Fig. 1. This process offers advantages over other synthesis techniques such as lower costs, better compositional homogeneity, higher purity, lower



Fig. 1. General illustration of $PbZrO_3$ powder synthesis prepared by the polymeric precursor method.

processing temperatures and the ability to coat larger substrate areas. In this method, zirconium citrates were formed by the dissolution of zirconium (IV) n-propoxide in an aqueous solution of citric acid at 60–70 °C.

After homogenization of the Zr solution, $PbNO_3$ was slowly added. In order to achieve total $PbNO_3$ dissolution, ammonium hydroxide was added drop by drop until the pH reached 7–8. Complete salt dissolution resulted in a clear solution. After complete dissolution of the $PbNO_3$ salt, ethylene glycol was added to promote polymerization of the mixed citrates by polyesterification. The molar ratio between the Pb and Zr cations was 1:1 and the citric acid/ethylene glycol ratio was fixed at 60/40 mass ratio. Heat treatment was carried out at various temperatures, from 300 to 800 °C for 2 h.

The PZ powders were structurally characterized by X-ray diffraction using a Rigaku D/Max-2400 diffractometer with Cu Kα radiation (λ = 1.5406 Å).

Infrared analysis was performed with an Equinox/55 (Bruker) Fourier transformed infrared (FT-IR) spectrometer. The FT-IR spectra of the powders were recorded at room temperature in the 400–3500 $cm^{-1}$ frequency range, allowing observation of the lattice vibration at different temperatures.

Raman data was recorded using an RFS/100 Bruker FT-Raman spectrometer with a Nd:YAG laser producing a 1064.0 nm excitation light. Spectral resolutions of 4 $cm^{-1}$ and 10–700 $cm^{-1}$ were analyzed.

The PL spectra were recorded at room temperature with a U1000 Jobin-Yvon double monochromator coupled to a cooled GaAs photomultiplier and a conventional photon counter. The 488.0 nm excitation wavelength of an argon ion laser, set to maximum power output of 20 mW, was used. A cylindrical lens was used to prevent the sample from overheating and the slit width was 100 mm. All measurements were taken at room temperature. The dependence of grain morphology and size on annealing time was analyzed by scanning electronic micro-scopy using a DSM-940A Zeiss scanning electron microscope (SEM).

## 3. Results and discussion

### 3.1. X-ray diffraction

Fig. 2(a)–(f) shows the X-ray-diffraction patterns of all PZ powder samples annealed at 300, 400, 500, 600, 700 and 800 °C for 2 h. Fig. 2(a)–(c) illustrates the XRD patterns for these samples. Here the patterns are typical of disordered material indicating incomplete powder crystallization. In Fig. 2(c) and (d), the XRD patterns consist of peaks that are characteristic of crystalline PZ while the pattern in Fig. 2(f) is that of a polycrystalline material.

XRD patterns revealed that all PZ diffraction peaks could be indexed to the orthorhombic perovskite phase without secondary phases. This is in agreement with the ICDD card #490001. Relative intensities and sharp diffraction peaks indicate that the PZs are well-crystallized, suggesting long-range order. However the structurally ordered PZs clearly start at temperatures of 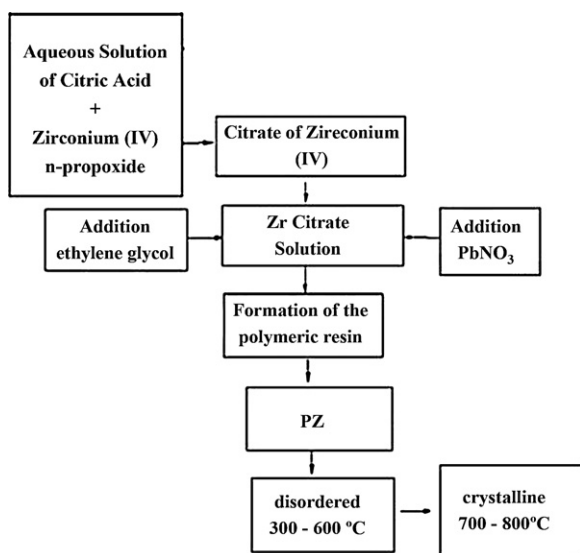500 and 600 °C and are completely ordered